101-710
102-8241
103-6643
104-270

UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	35.G2127
First Named Inventor or Application Identifier	
TOSHIO ICHIZAKI	
Express Mail Label No.	

69482 U.S. PTO 03/27/98

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

1. [X] Fee Transmittal Form *(Submit an original, and a duplicate for fee processing)*
2. [X] Specification — *Total Pages* 31
3. [X] Drawing(s) *(35 USC 113)* — *Total Sheets* 11
4. [X] Oath or Declaration — *Total Pages* 3
   - a. [ ] Newly executed (original or copy)
   - b. [X] Unexecuted for information purposes
   - c. [ ] Copy from a prior application (37 CFR 1.63(d)) *(for continuation/divisional with Box 17 completed)* ***[Note Box 5 below]***
     - i. [ ] DELETION OF INVENTOR(S) Signed Statement attached deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b)
5. [ ] Incorporation By Reference *(useable if Box 4c is checked)* The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4c, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
6. [ ] Microfiche Computer Program *(Appendix)*
7. Nucleotide and/or Amino Acid Sequence Submission *(if applicable, all necessary)*
   - a. [ ] Computer Readable Copy
   - b. [ ] Paper Copy (identical to computer copy)
   - c. [ ] Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

8. [ ] Assignment Papers (cover sheet & document(s))
9. [ ] 37 CFR 3.73(b) Statement *(when there is an assignee)* [ ] Power of Attorney
10. [ ] English Translation Document *(if applicable)*
11. [X] Information Disclosure Statement (IDS)/PTO-1449 [X] Copies of IDS Citations
12. [X] Preliminary Amendment
13. [X] Return Receipt Postcard (MPEP 503) *(Should be specifically itemized)*
14. [ ] Small Entity Statement(s) [ ] Statement filed in prior application Status still proper and desired
15. [ ] Certified Copy of Priority Document(s) *(if foreign priority is claimed)*
16. [ ] Other: _____

17. If a CONTINUING APPLICATION, *check appropriate box and supply the requisite information:*
    [ ] Continuation [ ] Divisional [ ] Continuation-in-part (CIP) of prior application No. ___/_____

18. CORRESPONDENCE ADDRESS

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CLAIMS	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
	TOTAL CLAIMS (37 CFR 1.16(c))	27-20 =	7	X $ 22.00 =	$154.00
	INDEPENDENT CLAIMS (37 cfr 1.16(b))	4-3 =	1	X $ 82.00 =	$82.00
	MULTIPLE DEPENDENT CLAIMS (if applicable) (37 CFR 1 16(d))			$270.00 =	$270.00
				BASIC FEE (37 CFR 1.16(a))	$790.00
			Total of above Calculations =		$1,296.00
	Reduction by 50% for filing by small entity (Note 37 CFR 1.9, 1.27, 1.28).				
				TOTAL =	$1,296.00

19. Small entity status

a. ☐ A Small entity statement is enclosed

b. ☐ A small entity statement was filed in the prior nonprovisional application and such status is still proper and desired.

c. ☐ Is no longer claimed.

20. ☒ A check in the amount of $ 1,296.00 to cover the filing fee is enclosed.

21. ☐ A check in the amount of $ _____ to cover the recordal fee is enclosed.

22. The Commissioner is hereby authorized to credit overpayments or charge the following fees to Deposit Account No. 06-1205:

a. ☒ Fees required under 37 CFR 1.16.

b. ☐ Fees required under 37 CFR 1.17.

c. ☐ Fees required under 37 CFR 1.18.

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED	
NAME	Leonard P. Diana, Registration No. 29,296
SIGNATURE	
DATE	March 26, 1998

F502\A595666

35.G2127 PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
	:	Examiner: Unassigned
TOSHIO ICHIZAKI	)	
	:	Group Art Unit: Unassigned
Application No.: Unassigned	)	
	:	
Filed: Herewith	)	
	:	
For: PRODUCTION APPARATUS AND METHOD OF FLUORIDE CRYSTAL, AND CRUCIBLE	)	March 26, 1998

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Prior to examination of the merits, please amend the above-identified application, filed herewith, as follows:

IN THE SPECIFICATION

Page 8, line 5, change "1 is a" to --1, consisting of FIGS. 1A and 1B, are-- and "view" to --views--;

line 15, change "4 is a" to --4, consisting of FIGS. 4A and 4B, are-- and "view" to --views--.

Page 9, line 5, change "10 is a" to --10, consisting of FIGS. 10A and 10B, are-- and "diagram" to --diagrams--;

line 9, after "process" insert -- in four steps--.

IN THE CLAIMS

Please amend Claims 6-11, 13 and 14 as follows:

Claim 6, line 1, change "4 or 5," to --4,--.

Claim 7, line 1, change "any of claims 4 to 6," to --claim 4,--.

Claim 8, line 1, change "any of claims 3 to 7," to --claim 3 or 4,--.

Claim 9, line 1, change "any of claims 3 to 8," to --claim 3 or 4,--.

Claim 10, line 1, change "any of claims 3 to 9," to --claim 3 or 4,--.

Claim 11, line 1, change "any of claims 3 to 10," to --claim 3 or 4,--.

Claim 13, line 3, delete " or 12".

Claim 14, line 2, change "any of claims 3 to 11," to --claim 3 or 4,--.

REMARKS

The specification has been amended to include a more exact list of the drawing figures that are part of the application. In addition, Claims 6-11, 13 and 14 have been amended to eliminate improper multiple dependencies.

Applicant's undersigned attorney may be reached in our New York office by telephone at (212) 758-2400. All correspondence should continue to be directed to our address listed below.

Respectfully requested,

Attorney for Applicant

Registration No. 29,284

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F502\A595678

TITLE OF THE INVENTION

PRODUCTION APPARATUS AND METHOD OF FLUORIDE CRYSTAL, AND CRUCIBLE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a production apparatus of a fluoride crystal preferable for various kinds of optical elements, lens, window materials, prisms, and the like to be used in a wide wavelength range from a vacuum ultraviolet region to a far infrared region, in particular, to a production apparatus of a fluoride crystal to be used for an optical material such as a large aperture lens (aperture of 250 mm or more) for an excimer laser.

Description of the Related Art

An excimer laser attracts attention as the only one high output laser to oscillate outside an ultraviolet region so that the application thereof is expected in the electronic industry, chemical industry, and energy industry.

Specifically, the excimer laser is used in processing metal, resin, glass, ceramics and

semiconductors, and a chemical reaction.

An apparatus for generating an excimer laser beam is known as an excimer laser oscillating apparatus. A laser gas filled in a chamber, such as Ar, Kr, Xe, F_2, Cl_2 is excited by the electron beam radiation or the electric discharge. The excited atoms bond with atoms in the ground state so as to produce molecules capable of existing only in the excited state. The molecules are the excimer. Due to its instability, the excimer immediately discharges the ultraviolet ray and falls into the ground state. This phenomenon is called the bond free transition. An apparatus for taking out a laser beam by amplifying the ultraviolet ray obtained by the transition in an optical resonator comprising a pair of mirrors is an excimer oscillating apparatus.

Among excimer laser beams, a KrF laser and an Arf laser have a wavelength of 248 nm and 193 nm, respectively in a vacuum ultraviolet ray region so that an optical system having a high transmissivity with respect to the wavelength region needs to be used. Examples of glass materials preferably used in the optical system include fluorides, such as calcium fluoride, magnesium fluoride, barium fluoride, neodymium fluoride, lithium fluoride, and lanthanum fluoride.

Hereinafter a conventional production method of a

fluoride crystal will be explained with reference to an example of calcium fluoride called fluorite, which can be represented by the stoichiometry ratio of CaF_2.

As conventional production methods of a fluoride crystal, methods disclosed in the official gazettes of Japanese Patent Laid-Open Nos. 4-349199 and 4-349198 can be presented. In short, in order to prevent the loss of weight in directly melting a high purity powdery material produced by a chemical synthesis due to the bulk specific gravity, the high purity material in a cullet state is used at the time of placing the same in a crystal growth furnace. Hereinafter the knowledge obtained by the present inventor to lead to the present invention will be described.

FIG. 11 is a schematic diagram showing the production method of a fluoride crystal initially conducted by the present inventor.

In the process S1, a powdery material is prepared. In the process S2, the material placed in a container is melted, and then cooled. In the process S3, solidified agglomerates are pulverized with a stainless steel pulverizer. In the post process S4, a fluorite block is produced by melting and gradually cooling the pulverized agglomerates placed in a crucible for the crystal growth.

The process S2 is conducted for reducing the bulk

specific density change before and after melting in the process S4, and further, for eliminating impurities in the material.

In the processes S2 and S4, a scavenger, which is a fluoride of a metal, is added in order to eliminate CaO produced by the reaction between the material (CaF_2) and water, and the like, or impurities originally existing in the material. For example, a ZnF_2 scavenger reacts with CaO so as to be ZnO and eliminated at the time of melting the crystals. As a result, the CaO impurities are eliminated so that a fluoride crystal having an excellent transmissivity characteristic can be obtained.

The fluoride crystal block accordingly obtained is cut in a desired thickness, processed and shaped to be a desired lens shape to be used as an optical material.

In the discussion of the production conditions for obtaining a fluoride crystal having a further high transmissivity by the present inventor, it was learned that the crucible structure cast a great influence on the optical characteristics of the crystal after growth.

That is, in the study on the relationship between the conventional crucible structure to be used in the refining process and the transmissivity of the crystal to be finally obtained, it was learned that although the amount is slight, impurities in a material and a reaction

product of a scavenger cannot be discharged to the outside but remain inside the crucible according to the crucible shape. The impurities deteriorate the optical characteristics of the final crystal, and generate the irregularity among the optical parts.

In the crystal growth process, a refined block needs to be pulverized and placed in a crucible. However, since the bulk density is lowered by the pulverization, a larger crucible is required for obtaining a desired crystal. Furthermore, due to the necessity of the pulverizing process, the productivity becomes poor. Moreover, a problem is involved in that a minute amount of impurities included at the time of the pulverization deteriorates the transmissivity of the crystal.

The present invention has been completed based on the knowledge and elaborate study for the solution of the problems. An object of the present invention is to provide a production apparatus of a fluoride crystal capable of producing a fluoride crystal having a high transmissivity, and efficiently eliminating impurities and a scavenger remained in the crystal.

Another object of the present invention is to provide a production apparatus of a fluoride crystal with a high productivity.

SUMMARY OF THE INVENTION

In order to solve the above-mentioned problems, the below-mentioned inventions are provided.

A first aspect of the present invention is a production apparatus of a fluoride crystal having a crucible divided in a plurality to have multi-stages, to be used for refining a material in a process for refining the material by adding a scavenger in the material.

A second aspect of the present invention is the production apparatus of a fluoride crystal having a degassing hole on a side wall portion of the crucible.

A third aspect of the present invention is a crucible having at least two degassing holes on a side wall portion.

A fourth aspect of the present invention is the crucible having a connecting hole in the bottom center portion, and having at least two degassing holes on a side wall portion.

A fifth aspect of the present invention is the crucible with the degassing holes having a diameter of 1 to 5 mm.

A sixth aspect of the present invention is the crucible with the connecting hole having a diameter of 1 to 5 mm.

A seventh aspect of the present invention is the

crucible with the area of the degassing holes smaller than the area of the connecting hole.

An eighth aspect of the present invention is the crucible with the degassing holes point symmetric with respect to the central axis of the crucible.

A ninth aspect of the present invention is the crucible having a cylindrical shape with the bottom face.

A tenth aspect of the present invention is the crucible having a 250 mm or more inner diameter.

An eleventh aspect of the present invention is the crucible having a region for mounting a material.

A twelfth aspect of the present invention is a multi-stage crucible having a region obtained by superimposing a plurality of the crucibles to be used as the region for mounting a material, and having a crucible without a connecting hole at the lowermost stage.

A thirteenth aspect of the present invention is a crystal production method for producing a calcium fluoride crystal using the crucible.

A fourteenth aspect of the present invention is a crystal production apparatus having the crucible.

A fifteenth aspect of the present invention is a crystal production apparatus having the multi-stage crucible.

A sixteenth aspect of the present invention is a

crucible having a plurality of the crucibles superimposed in multi-stages via a gap for a gas passage.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view showing an embodiment of a crucible to be used in a refining furnace of a production apparatus of a fluoride crystal of the present invention.

FIG. 2 is a schematic cross-sectional view showing an embodiment of a refining furnace preferably used in the present invention.

FIG. 3 is a schematic cross-sectional view showing an embodiment of a crystal growth furnace preferably used in the present invention.

FIG. 4 is a schematic cross-sectional view showing an embodiment of a growth furnace crucible preferably used in the present invention.

FIG. 5 is a schematic cross-sectional view showing an embodiment of an annealing furnace preferably used in the present invention.

FIG. 6 is a flow chart of a crystal production process preferably used in the present invention.

FIG. 7 shows a spectral transmissivity of a fluorite.

FIG. 8 is a schematic diagram of an exposing device

applied with optical parts of the present invention.

FIG. 9 is a projection optical system of an exposing device applied with optical parts of the present invention.

FIG. 10 is a schematic diagram of an excimer laser oscillator applied with optical parts of the present invention.

FIG. 11 is a schematic diagram showing a conventional fluorite production process.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 2 shows a refining furnace of a large aperture (aperture 250 mm or more) production apparatus of a fluoride crystal of the present invention. A crucible thereof is shown in FIG. 1 in detail. The present invention is not limited to the production of a fluoride crystal with a 250 mm or more aperture. Further, the present invention is also preferable for the production of an extremely large aperture fluoride of about 500 mm aperture.

In FIG. 2, numeral 201 represents a chamber of the refining furnace, which is connected to a vacuum exhaust system. Numeral 202 represents an insulating material, 203 a heater, and 204 a crucible, respectively.

As shown in FIGS. 1A and 1B, the crucible for a

refining furnace of the present invention is divided in a plurality, and superimposed in multi-stages. Numeral 100 represents a crucible main body, and 101 a lid for preventing evaporation of a material, respectively. Although the number of stages shown in an embodiment in FIG. 1 is three, it can be two or four or more. The entire surface of the crucible main body 100 and the lid 101 has minute unevenness so that even when the lid 101 covers the crucible main body 100, the inside of the crucible main body 100 is not closed completely. Further, similarly, the adjacent crucibles have a minute gap allowing the gas passage formed therebetween.

The size of the crucibles of each stage to be used in the present invention depends on the size of the fluoride crystal to be obtained. For example, since a crystal with about 250 mm to 500 mm aperture and about 10 mm to 100 mm thickness is needed in the case of a lens for an exposing device, a crucible with about 250 mm to 550 mm inner diameter and about 30 mm to 300 mm inner height is preferable. When a thin crystal is needed, the inner height can be 10 mm to 50 mm. When a crystal with a further smaller aperture is needed, the inner diameter can be smaller than 250 mm, for example, 80 mm to 100 mm.

In the present invention, the inner height of the crucible of each stage can be determined further

preferably according to the state of the material such that the height of the molten material becomes 50 mm or less.

With the height in the molten state of 50 mm or less, impurities which easily remain inside the crystal such as a metal element of a scavenger and oxygen can be efficiently discharged to the outside so that the impurity concentration in the crystal can be further lowered.

Further, by having multi-stages, crystals with a preferable size can be obtained for the number of the stages at the same time so that the productivity can be improved. By having a size accommodated in a growth furnace crucible in the next process, since it can be placed in the growth furnace as it is so that a pulverization process is not needed, the productivity can be improved.

The crucible shown in FIG. 1B has degassing holes 102 on the crucible side face in each stage. An impurity gas such as a scavenger can be discharged from the gap between the crucibles or the crucible and the lid in the configuration of FIG. 1A. With the configuration of FIG. 1B, the gas can be discharged mainly from the degassing holes 102. By providing the degassing holes 102, the discharge of the impurity gas is facilitated so that a

crystal of a further higher purity can be obtained. The size of the degassing holes 102 is preferably 1 to 5 mmθ. And it is preferable to provide the degassing holes symmetrically on the crucible side wall.

Hereinafter a production apparatus of the present invention and a production method of a calcium fluoride crystal as a fluoride will be explained.

(Material preparation)

As fluoride materials, fluorite ores and synthetic fluoride materials can be used. In the present invention, the latter can be used preferably.

(Mixing process)

A calcium fluoride material and a scavenger are mixed. At the time, it is preferable to mix by placing the calcium fluoride material and the scavenger in a container and rotating the container. Examples of scavengers include cadmium fluoride, lead fluoride, zinc fluoride, bismuth fluoride, sodium fluoride, and lithium fluoride. As the scavenger, those which can bond with oxygen easily compared with a fluoride to be grown, can be eliminated by the reaction with an oxide contained in the synthetic fluoride material, can provide a high purity, and cannot influence optical characteristics even when a minute amount thereof remains, are selected. Among these examples, zinc fluoride and bismuth fluoride

are particularly preferable.

The amount of a scavenger is preferably from 0.04 mol% to 5 mol%, more preferably from 0.1 to 1 mol%. The range is advantageous in that generated ZnO, and the like can be eliminated in a high temperature condition in each process, and that even when a minute amount thereof remains, optical characteristics can hardly be influenced.

(Refining process)

The mixed fluoride material is placed in a multi-stage crucible having a desired size in each stage, melted, and crystallized.

The melting temperature can be a melting point of the fluoride or higher. Preferably it is 1390 to 1450°C.

A thermocouple made from platinum (not illustrated) was used for measuring the temperature. The crucible temperature was measured with the thermocouple in the vicinity of the outer wall of the crucible. By the detailed study of the present inventor, it was learned that the measured temperature in the range from 1380 to 1450°C was preferable.

That is, with a temperature lower than 1380°C, the actual temperature in the crucible is low. If the temperature is close to the melting point, it takes a long time to completely melt the material so that the

productivity cannot be improved. On the other hand, with a temperature higher than 1450°C, the fluoride material can be evaporated drastically so that the decline of the productivity by the material loss cannot be avoided.

With the height of a melting liquid in each stage of 50 mm or less, an added scavenger, a reaction product, and the other impurities can be discharged easily.

Crystallization is conducted by gradually cooling the molten fluoride. The fluoride to be obtained in this stage is not necessarily single crystalline but can be polycrystalline. The surface layer of the obtained fluoride crystal is eliminated by 1 to 2 mm. It is also possible to conduct crystallization by cooling while lowering the crucible. In this case, the impurities can be eliminated further effectively.

(Crystal growth process)

In the crystal growth process, a refined fluoride crystal is placed in a growth furnace crucible having a diameter larger than the refining crucible alone or in a plurality in a superimposed state. It is preferable that the size (diameter) of the fluoride crystal obtained in the refining furnace crucible is 0.9 to 0.95 times as large as the size (diameter) of the growth furnace crucible. That is, it is preferable that the ratio of the size (diameter) of the fluoride obtained in the

refining furnace and the size (diameter) of the growth furnace crucible is 1:1.05 to 1:1.1. As mentioned above, since the crucible surface has minute unevenness, the fluoride crystal can be taken out easily from the refining furnace crucible. Further, the taken-out fluoride crystal can be placed in the growth furnace crucible without pulverization.

In the crystal growth process, it is preferable to eliminate calcium oxide by adding a scavenger in the growth furnace crucible with the fluoride crystal.

FIG. 3 is a schematic diagram showing a growth furnace to be used in the crystal growth process. In FIG. 3, numeral 301 represents a chamber for the growth furnace, 302 an insulating material, 303 a heater, 304 a crucible, 305 a fluoride and 306 a crucible lowering mechanism.

It is preferable that the growth furnace crucible is a multi-stage crucible like the refining furnace crucible as shown in FIG. 4 since the impurities in a material and a scavenger reaction product can be eliminated efficiently so that impurities in the crystal to be finally obtained can be further restrained, a crystal with a high transmissivity can be obtained.

FIG. 4A shows a multi-stage crucible with the simplest configuration of the present invention.

In the present invention, it is preferable to determine the internal height of the crucible in each stage according to the state of the material such that the height of the crystal block to be produced becomes 10 mm to 50 mm. Since the height of the crystal block becomes the internal height of the crucible in the configuration of FIG. 4B or 4C having connecting holes 402, it is preferable that the internal height of the crucible is 10 mm to 50 mm. With the height of not more than 50 mm, impurities which tends to remain inside a crystal, such as a metal element of a scavenger or oxygen can be discharged efficiently to the outside so that the impurity concentration in the crystal can be further lowered. On the other hand, with the height of not less than 10 mm, a crystal with a further lower defect density can be obtained. That is, according to the defect evaluation by the etch pit density of a cleavage plane, defect is conspicuous in the vicinity of the crystal bottom face. In order to reduce the influence, it is preferable to have the height of 10 mm or more.

Further, with the internal height of the crucible the same as the thickness of the optical part to be produced, a subsequent cutting process can be eliminated to improve the productivity. The crucible internal height of each stage is not necessarily the same, but

crucibles with different internal heights can be superimposed.

The crucible shown in FIG. 4B has a connecting hole 402 at the center part of the crucible bottom face in each stage. Through the hole, a molten liquid drops to the lower stage at the time of melting a material so that the stages communicate with each other. The size of the connecting holes 402 is preferably 1 to 5 mm diameter so that the molten liquid can drop to the lower stage while overcoming the surface tension.

The crystallization proceeds from the lowermost stage. The crystal of the connecting hole 402 serves as the seed to cause the crystal growth in the upper stages subsequently so as to provide a crystal with an excellent crystal quality.

A gas in the crucible can be discharged to the outside from the superimposing portions 404 of each stage. By selecting a material not wettable by a molten liquid such as black lead for the crucible, leakage of the molten liquid from the superimposing portions 404 can be prevented. However, since leakage is liable in the lower stages by the pressure with a large number of crucible stages, it is preferable to have a level difference in the superimposing portions 404 as shown in the figure.

The configuration of FIG. 4C is further provided with degassing holes 403 in the vicinity of the bottom face. By the degassing holes 403, an impurity gas can be discharged further easily so that a crystal with a higher purity can be obtained. The size of the degassing holes 403 is preferably smaller than the diameter of the above-mentioned connecting holes 402, and it is preferable to provide the degassing holes 403 symmetrically.

After heating the crucible to about 1390 to 1450°C so as to melt the fluoride, the crucible is lowered at the rate of about 0.1 to 5.0 mm/h. Even though the crucible is not actively cooled, the temperature of a part of the fluoride is lowered according to the lowering movement of the crucible so as to be crystallized.

(Annealing process)

The fluoride crystal after the crystal growth is applied with a heat treatment. In the annealing process, the crucible is heated to 900 to 1000°C. The heating time is preferably 20 hours or more.

FIG. 5 is a schematic diagram showing an annealing furnace to be used in the annealing process. In FIG. 5, numeral 501 represents a chamber of an annealing furnace, 502 an insulating material, 503 a heater, 504 a crucible and 505 a fluoride crystal.

(Processing)

The obtained product will be shaped according to an optical material to be provided (convex lens, concave lens, disk shape, plate shape, and the like). As needed, a reflection preventing film can be provided on the surface of the optical material of the fluoride crystal. As the reflection preventing film, magnesium fluoride, aluminum oxide, and tantalum oxide can be used preferably. These can be formed by deposition with the resistance heating, electron beam deposition, or sputtering. Since an optical material obtained by the present invention hardly contains water, the reflection preventing film can be attached with an excellent adherence.

By combining various kinds of lenses accordingly obtained, an optical system appropriate for an excimer laser, in particular, an ArF excimer laser can be provided. Furthermore, an exposing device can be provided by combining an excimer laser light source, an optical system having a lens made from calcium fluoride and a stage capable of moving a substrate.

Hereinafter an exposing device applied with an optical material of the prevent invention will be explained.

Examples of exposing devices include a reduction projection exposing device and a lens type equivalent

magnification projection exposing device.

In particular, in order to expose the entire surface of a wafer, a stepper applied with a step and repeat method, where after exposing one small section (field) of the wafer, an adjacent one field is exposed by moving the wafer by one step, is preferable. Of course it can be preferably used in an exposing device with a micro scan method.

FIG. 8 shows a schematic configuration of an exposing device of the present invention. In FIG. 8, numeral 21 represents a illumination light source portion and 22 an exposing mechanism portion, which are provided independently. That is, they are physically separated. Numeral 23 represents an illumination light source, such as a high output large light source like an excimer laser. Numeral 24 represents a mirror, 25 a concave lens, and 26 a convex lens, respectively. 25 and 26 also serve as a beam expander for expanding the beam diameter of a laser to about a size of an optical integrator. Numeral 27 represents a mirror, and 28 an optical integrator for evenly illuminating on a reticle. The illumination light source portion 21 comprises from the laser 23 to the optical integrator 28. Numeral 29 represents a mirror and 30 a condenser lens for collimating a light flux outputted from the optical

integrator. Numeral 31 represents a reticle with a circuit pattern formed whereon, 31a a reticle holder for holding the reticle, 32 a projection optical system for projecting the reticle pattern, and 33 a wafer where the reticle 31 pattern is printed at the projecting lens 32. Numeral 34 represents an XY stage for holding the wafer 33 and moving in the XY directions at the time of printing. Numeral 35 represents a fixed table of the exposing device.

The exposing mechanism portion 22 comprises from the mirror 29 to the fixed table 35, which are a part of the illumination optical system. Numeral 36 represents an alignment means to be used for the TTL alignment. In general, an exposing device further comprises an auto focus mechanism, a wafer conveyance mechanism, and the like. These are also included in the exposing mechanism portion 22.

FIG. 9 shows an example of an optical material to be used in an exposing device of the present invention, which can be used in the projection optical system of the exposing device shown in FIG. 8. The lens assembly comprises 11 lenses L1 to L11 without bonding to each other. An optical material made of a fluorite of the present invention can be used as a lens or a mirror shown in FIG. 9 or 10, or a mirror or a lens of a mirror type

exposing device (not illustrated). It is more preferable to provide a reflection preventing film or an amplifying reflection film on the surface of a lens or a mirror.

Furthermore, an optical part made from a fluoride crystal of the present invention can be used as a prism or an etalon.

FIGS. 10A and 10B are schematic diagrams of a configuration of an excimer laser oscillator using an optical part made of a fluoride crystal of the present invention.

The excimer laser oscillator shown in FIG. 10A comprises a resonator 83 for emitting and resonating an excimer laser, an hole 82 for adjusting the excimer laser outputted from the resonator 83, a prism 84 for having narrowing the band width of the excimer laser light, and a reflecting mirror 81 for reflecting the excimer laser.

The excimer laser oscillator shown in FIG. 10B comprises a resonator 83 for emitting and resonating an excimer laser, an hole 82 for adjusting the excimer laser outputted from the resonator 83, an etalon for having the wavelength of the excimer laser to be single, and a reflection mirror for reflecting the excimer laser.

An excimer laser beam oscillator comprising a fluoride crystal of the present invention as a prism or a etalon can have a further smaller excimer laser

wavelength via the prism or the etalon, in other words, can have the wavelength of the excimer laser to be single.

By radiating an excimer laser beam to a photosensitized resist on a substrate via a reticle pattern with the exposing device, a latent image corresponding to the pattern to be formed can be provided.

Example

A production apparatus of a fluoride crystal of the present invention will be explained concretely with reference to examples.

Example 1

In this example, a calcium fluoride crystal was produced according to a procedure shown in FIG. 6. Hereinafter each process will be explained.

(Prescription, mixing process)

A powdery calcium fluoride material was placed in a container. 0.08 mol% of a scavenger (ZnF_2) was measured based on the material, and added to the container with the material. The container used has a capacity about double as much as the volume of the material. The material and the scavenger were mixed by rotating the container for about 1 hour.

(Refining process)

The material was refined with a refining furnace shown in FIG. 2.

A multi-stage crucible shown in FIG. 1A with three stages was used.

After filling the prepared material in each stage of the crucible, the crucible was set in the refining furnace. By vacuum-exhausting the inside of the chamber 201, the moisture in the material 205 was eliminated.

While maintaining the vacuum degree at 5×10^{-4} Torr or less until the temperature where the material starts melting, the crucible 204 was heated by the heater 203. The material was melted at 1390 to 1450°C. The material filled in the crucible was completely melted.

After reaching the melting temperature, the crucible was maintained until the vacuum degree becomes 2×10^{-6} Torr or less.

Then, the crucible was cooled down by turning off the power of the heater to about the room temperature. The fluoride crystals were taken out from each stage and the surface layer thereof was eliminated by about 1 mm.

(Crystal growth process)

Then the crystal growth of the calcium fluoride was conducted with the growth furnace shown in FIG. 3.

ZnF_2 was placed in the crucible 304 as the scavenger. Further, a plurality of the refined crystal blocks were

placed in each crucible stage in a superimposed stage. Then, the crucible was set in the growth furnace. The amount of the ZnF_2 scavenger was 0.02 mol% with respect to the refined crystal blocks.

The inside of the chamber 301 was vacuum-exhausted to eliminate the moisture in the crystals 305. Then the crucible was heated by the heater 303 while maintaining the vacuum degree at 5×10^{-4} Torr or less until the temperature where the material starts melting. The material was melted at 1390 to 1450°C. The material filled in the crucible was completely melted.

After reaching the melting temperature, the crucible was maintained until the vacuum degree becomes 2×10^{-6} Torr or less. Further, the crucible was maintained for about 10 hours after the temperature reaches a stable state.

The crucible was moved downward by the lowering mechanism 306 at about 2 mm/hour rate. When the crucible was completely lowered, the voltage applied to the heater 303 was gradually reduced such that the temperature lowering rate becomes within about 100°C/hour.

The power of the heater was switched off to cool down to about the room temperature. The calcium fluoride crystal (50 mm thickness) was taken out from the furnace.

(Annealing process)

With the annealing furnace shown in FIG. 5, the calcium fluoride crystal was heat-treated. The taken-out crystal was set in the annealing crucible 504. About 0.04 mol% of ZnF_2 with respect to the crystal was sprinkled substantially evenly as the scavenger between the crystal and the crucible. The inside of the chamber 501 was vacuum-exhausted and gradually heated. The temperature schedule was as mentioned below.

Room temperature → 900°C (rising rate + 100°C/h)

Maintain at 900°C (20 hours)

900°C → room temperature (lowering rate − 6°C/h)

After cooling to about the room temperature, the crystal was taken out from the furnace.

The crystal accordingly produced was cut in a 10 mm thickness and abraded.

Example 2

In this embodiment, a fluoride crystal was produced in the process the same as Example 1 except that the crucible shown in FIG. 1B was used instead of the crucible of the refining furnace of Example 1. The degassing holes with a 3 mm diameter were provided at 8 positions symmetrically.

Example 3

In this embodiment, a fluoride crystal was produced in the process the same as Example 1 except that the

multi-stage crucible with the configuration of FIG. 4B was used as the growth furnace crucible.

Example 4

In this embodiment, a fluoride crystal was produced in the process the same as Example 2 except that a crucible having substantially the same configuration as the crucible shown in FIG. 4B was used.

Conventional Example

In order to evaluate the performances of the fluoride crystals obtained in Examples 1 to 4, a calcium fluoride crystal was produced as the comparative example in the process the same as Example 1 except that a block produced in the conventional production process explained with reference to FIG. 11 excluding the process for eliminating an impurity gas was pulverized and used as the material.

The spectral transmissivity of the fluorites produced in Examples 1 to 4 and Conventional Example are shown in FIG. 7.

As apparent from the comparison between Example 1 and Conventional Example, by using a multi-stage crucible having a gap to allow the passage of a gas between crucibles for the refining furnace, the transmissivity of the crystal to be finally obtained becomes higher in the short wavelength region. It was also learned that the

spectral transmissivity can be further improved in Example 2 where degassing holes are provided in the crucible side face for the refining furnace.

Furthermore, it was learned that the spectral transmissivity can be further higher in Examples 3 and 4 with a multi-stage crucible for the growth furnace compared with the corresponding Examples 1 and 2.

As mentioned above, according to the present invention, since a scavenger and the other impurity gases can be eliminated efficiently from the crystal, a fluoride crystal with a high transmissivity can be obtained.

Accordingly, even when a short wavelength light beam of a high output is radiated repeatedly over a long period, a highly reliable fluoride crystal without the risk of deteriorating the transmissivity characteristics can be provided.

Furthermore, according to the present invention, since the refined crystal can be placed in the growth furnace as it is, the productivity can be improved so that an optical material can be produced at a low cost.

WHAT IS CLAIMED IS:

1. A production apparatus of a fluoride crystal having a crucible divided in a plurality to have multi-stages, to be used for refining a material in a process for refining the material by adding a scavenger in the material.

2. The production apparatus of a fluoride crystal according to claim 1, wherein a degassing hole is provided on a side wall portion of the crucible.

3. A crucible having at least two degassing holes on a side wall portion.

4. A crucible having a connecting hole in the bottom center portion, and at least two degassing holes on a side wall portion.

5. The crucible according to claim 3 or 4, wherein the degassing holes have a diameter of 1 to 5 mm.

6. The crucible according to claim 4 or 5, wherein the connecting hole has a diameter of 1 to 5 mm.

7. The crucible according to any of claims 4 to 6, wherein the area of the degassing holes is smaller than the area of the connecting hole.

8. The crucible according to any of claims 3 to 7, wherein the degassing holes are point symmetric with respect to the central axis of the crucible.

9. The crucible according to any of claims 3 to 8, having a cylindrical shape with the bottom face.

10. The crucible according to any of claims 3 to 9, having a 250 mm or more inner diameter.

11. The crucible according to any of claims 3 to 10, having a region for mounting a material.

12. A multi-stage crucible having a region obtained by superimposing a plurality of the crucibles according to claim 3 or 4 as the region for mounting a material, and having a crucible without a connecting hole at the lowermost stage.

13. A crystal production method for producing a calcium fluoride crystal using the crucible according to claim 11 or 12.

14. A crystal production apparatus having the crucible according to any of claims 3 to 11.

15. A crystal production apparatus having the multi-stage crucible according to claim 12.

16. A crucible having a plurality of the crucibles superimposed in multi-stages via a gap for a gas passage.

ABSTRACT OF THE DISCLOSURE

An object of the present invention is to provide a production apparatus and method of a fluoride crystal, and a crucible for the growth capable of efficiently eliminating impurities and a scavenger remained in the crystal so as to produce a fluoride crystal with a high transmissivity. A crucible divided into a plurality to have multi-stages is used for refining a material in the material refining process by adding a scavenger in the material. Further, a degassing hole was provided to the side wall portion of the crucible. A crucible of the present invention has at least two degassing holes at the side wall portion. Further, a crucible of the present invention has a connecting hole at the center part of the bottom face with at least two degassing holes in the side wall portion.

COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

(Page 1)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled PRODUCTION APPARATUS AND METHOD OF FLUORIDE CRYSTAL, AND CRUCIBLE,

the specification of which [X] is attached hereto [ ] was filed on _____ as United States Application No. or PCT International Application No. _____ and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b), of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designates at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate, or PCT international application having a filing date before that of the application on which priority is claimed:

Country	Application No.	Filed (Day/Mo./Yr.)	(Yes/No) Priority Claimed
Japan	081624/1997	March 31, 1997	Yes
Japan	Unassigned	February 27, 1998	Yes

COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

(Page 2)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

Application No.	Filed (Day/Mo./Yr.)	Status (Patented, Pending, Abandoned)

I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Joseph M. Fitzpatrick (Registration No. 17,398), Lawrence F. Scinto (Registration No. 18,973), William J. Brunet (Registration No. 20,452), Robert L. Baechtold (Registration No. 20,860), John A. O'Brien (Registration No. 24,367), John A. Krause (Registration No. 24,613), Henry J. Renk (Registration No. 25,499), Peter Saxon (Registration No. 24,947), Anthony M. Zupcic (Registration No. 27,276), Charles P. Baker (Registration No. 26,702), Stevan J. Bosses (Registration No. 22,291), Edward E. Vassallo (Registration No. 29,117), Ronald A. Clayton (Registration No. 26,718), Lawrence A. Stahl (Registration No. 30,110), Laura A. Bauer (Registration No. 29,767), Leonard P. Diana (Registration No. 29,296), Nicholas N. Kallas (Registration No. 31,530), William M. Wannisky (Registration No. 28,373), Lawrence S. Perry (Registration No. 31,865), Robert H. Fischer (Registration No. 30,051), Christopher Philip Wrist (Registration No. 32,078). Gary M. Jacobs (Registration No. 28,861), Michael K. O'Neill (Registration No. 32,622), Bruce C. Haas (Registration No. 32,734), Scott K. Reed (Registration No. 32,433), Scott D. Malpede (Registration No. 32,533), Fredrick M. Zullow (Registration No. 32,452), Richard P. Bauer (Registration No. 31,588), Warren E. Olsen (Registration No. 27,290), Abigail F. Cousins (Registration No. 29,292), Steven E. Warner (Registration No. 33,326), Thomas J. O'Connell (Registration No. 33,202), David L. Schaeffer (Registration No. 32,716), Jack S. Cubert (Registration No. 24,245), Mark A. Williamson (Registration No. 33,628), Jean K. Dudek (Registration No. 30,938), Raymond R. Mandra (Registration No. 34,382), Dominick A. Conde (Registration No. 33,856), Pasquale A. Razzano (Reg. No. 25,512), John W. Behringer (Registration No. 23,086), Robert C. Kline (Registration No. 17,739), Mark J. Itri (Registration No. 36,171), Michael P. Sandonato (Registration No. 35,345), Jack M. Arnold (Registration No. 25,823), John D. Carlin (Registration No. 37,292), Daniel S. Glueck (Registration No. 37,838), Joseph W. Ragusa (Registration No. 38,586), Brian L. Klock (Registration No. 36,570), Anne M. Maher (Registration No. 38,231), Thomas D. Pease (Registration No. 35,317), Bruce M. Wexler (Registration No. 35,409), Robert S. Mayer (Registration No. 38,544), Errol B. Taylor (Registration No. 39,853), Matthew J. Golden (Registration No. 35,161), Sean W. O'Brien (Registration No. 37,689), Dolores A. Moro-Grossman (Registration No. 33,972), T. Thomas Gellenthien (Registration No. 39,683), Douglas Sharrott (Registration No. 39,832), Gordon F. Sieckmann (Registration No. 28,667), Jay H. Anderson (Registration No. 38,371), Nandu A. Talwalkar (Registration No. 41,339), Leonard J. Santisi (Registration No. 24,135), Shu Muk Lee (Registration No. 41,147), Kathryn L. Sieburth (Registration No. 40,072), Lee A. Goldberg (Registration No. 38,894), and Leisa M. Smith (Registration No. 39,378).

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COMBINED DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATION
(Page 3)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor's signature _____

Date _____ Citizen/Subject of Japan

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Full Name of Second Joint Inventor, if any _____

Second Inventor's signature _____

Date _____ Citizen/Subject of _____

Residence _____

Post Office Address _____

Full Name of Third Joint Inventor, if any _____

Third Inventor's signature _____

Date _____ Citizen/Subject of _____

Residence _____

Post Office Address _____

Full Name of Fourth Joint Inventor, if any _____

Fourth Inventor's signature _____

Date _____ Citizen/Subject of _____

Residence _____

Post Office Address _____

FIG. 1A

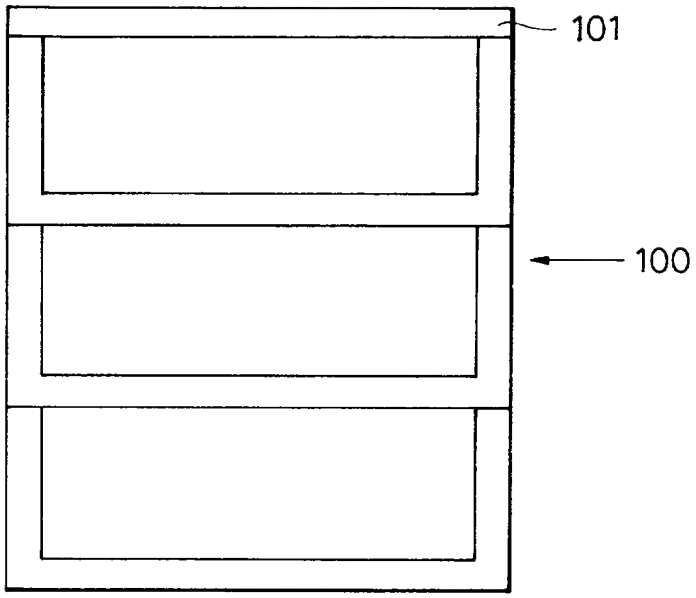

FIG. 1B

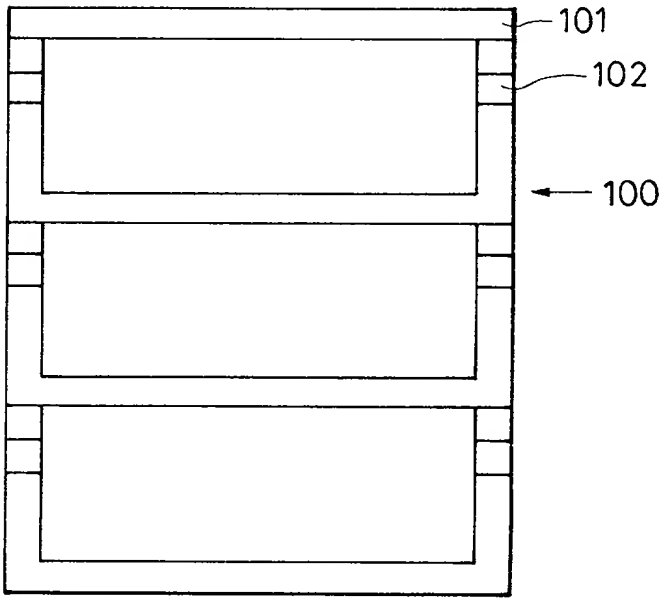

FIG. 2

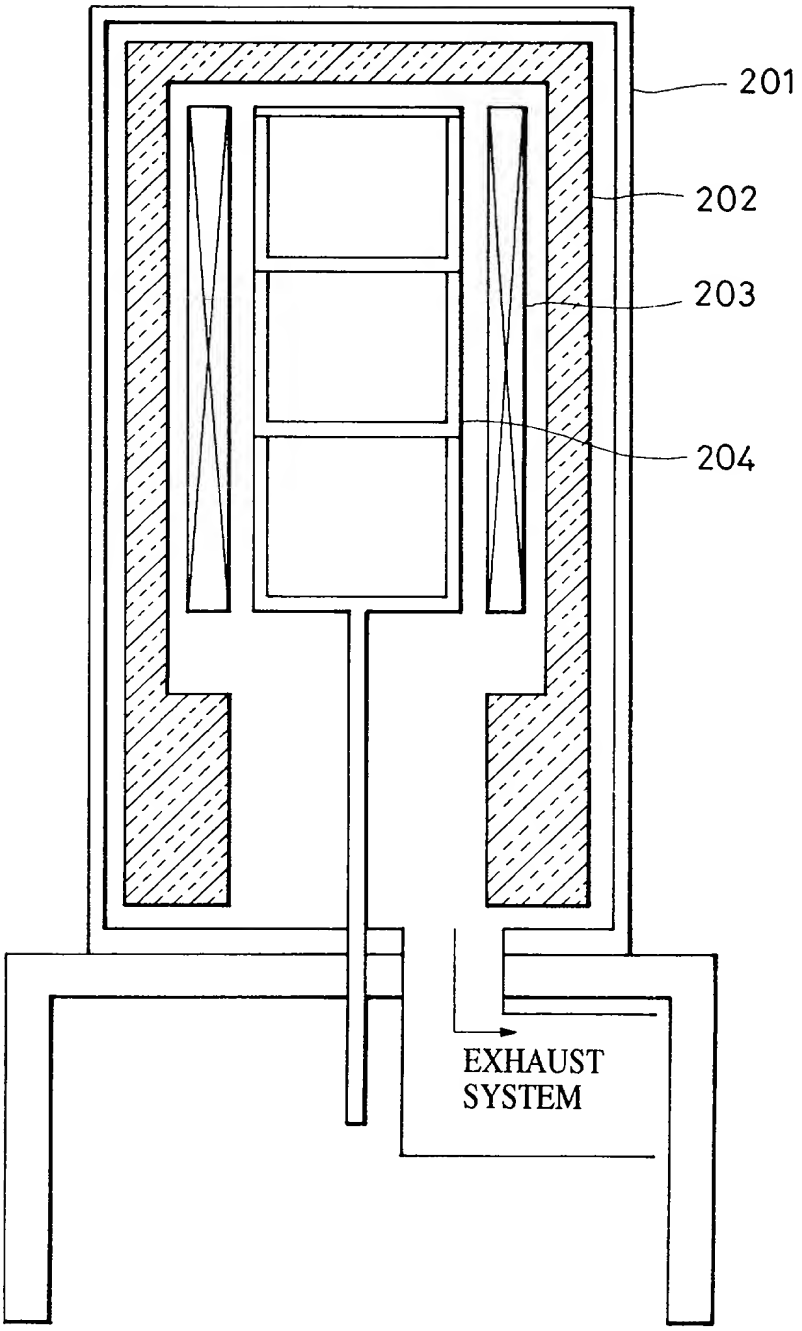

FIG. 3

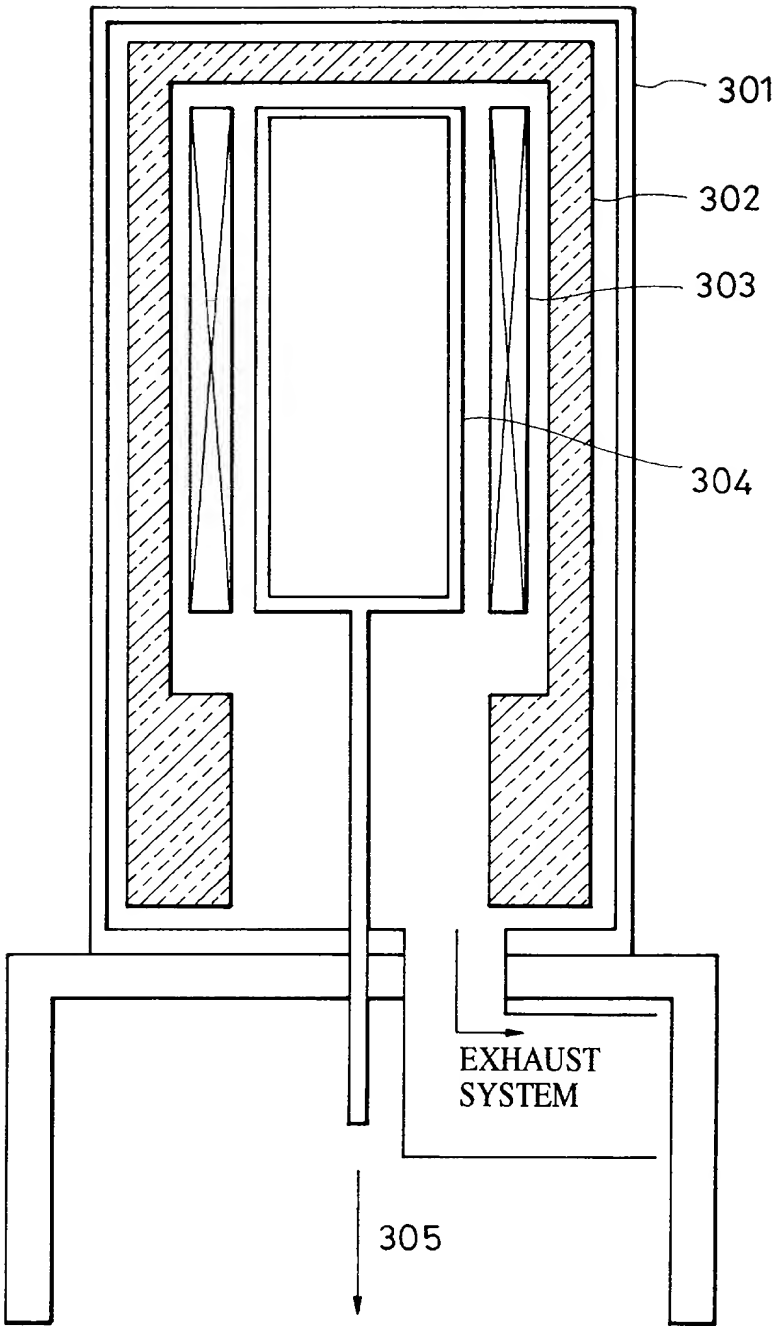

FIG. 4A

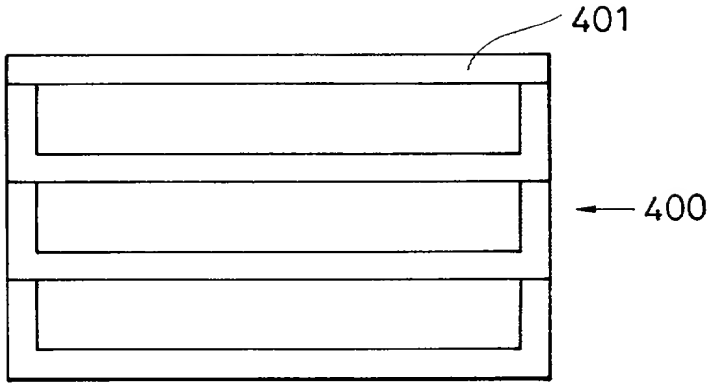

FIG. 4B

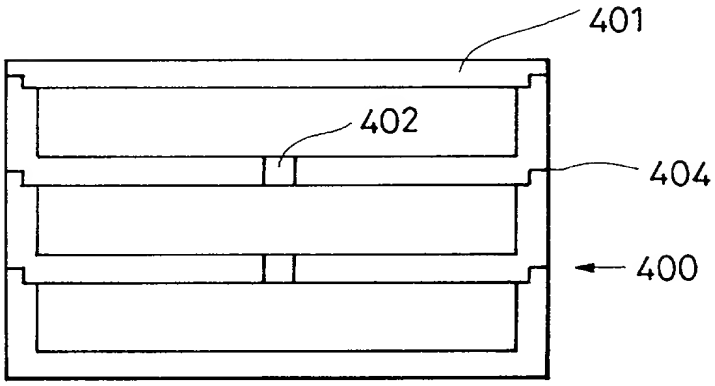

FIG. 4C

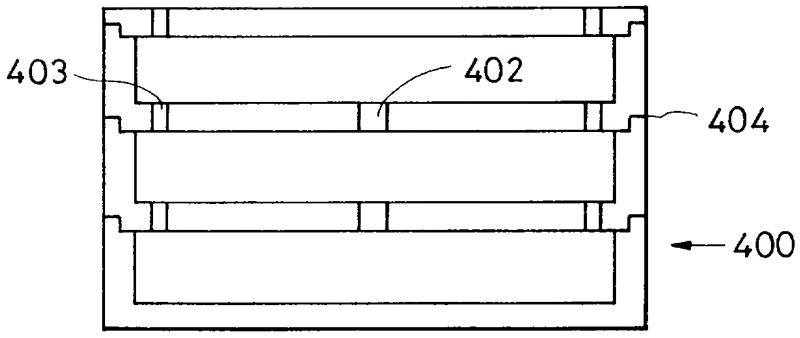

FIG. 5

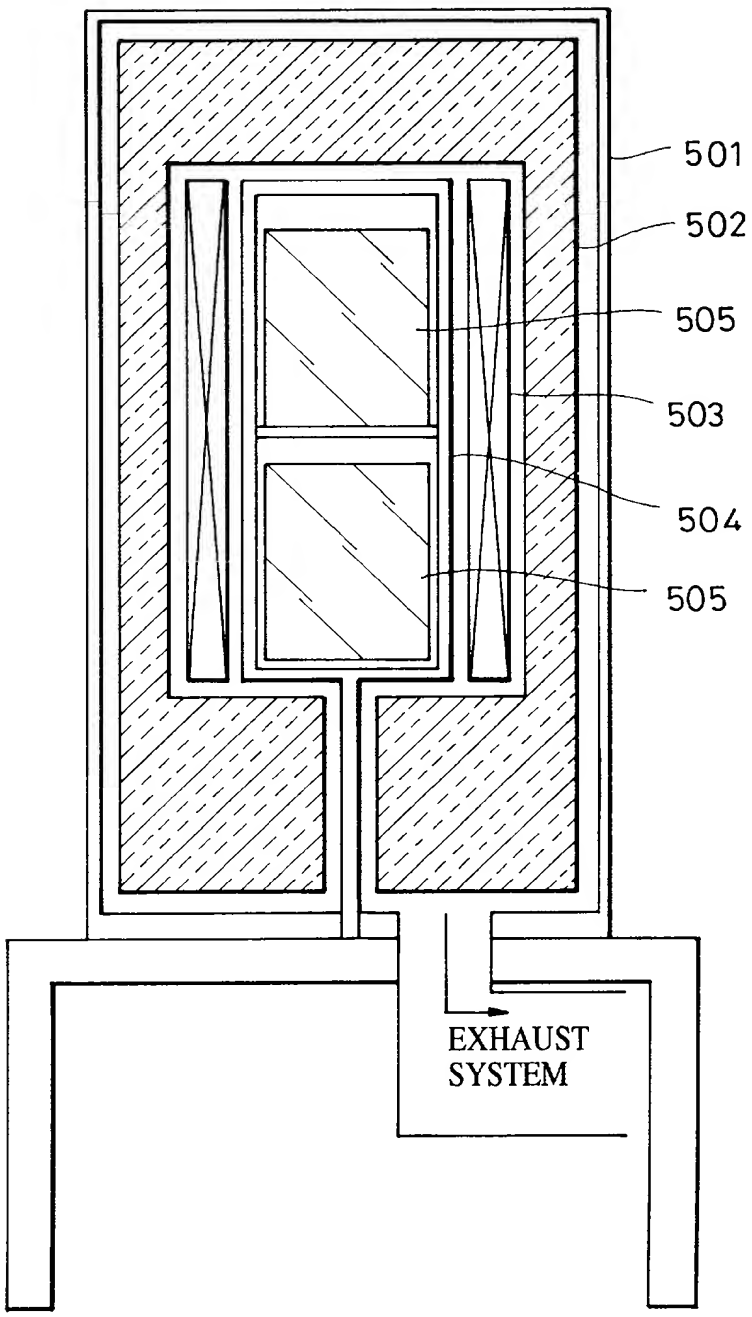

FIG. 6

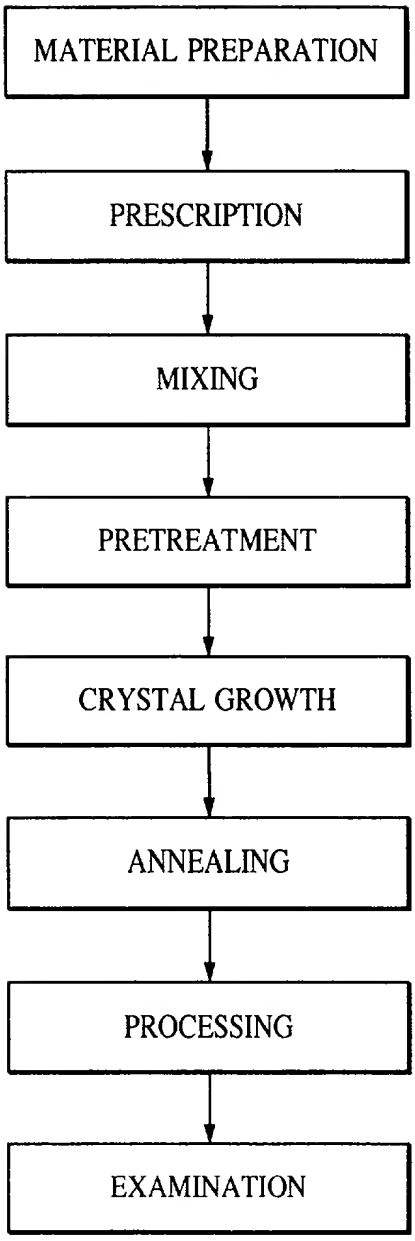
MATERIAL PREPARATION
PRESCRIPTION
MIXING
PRETREATMENT
CRYSTAL GROWTH
ANNEALING
PROCESSING
EXAMINATION

FIG. 7

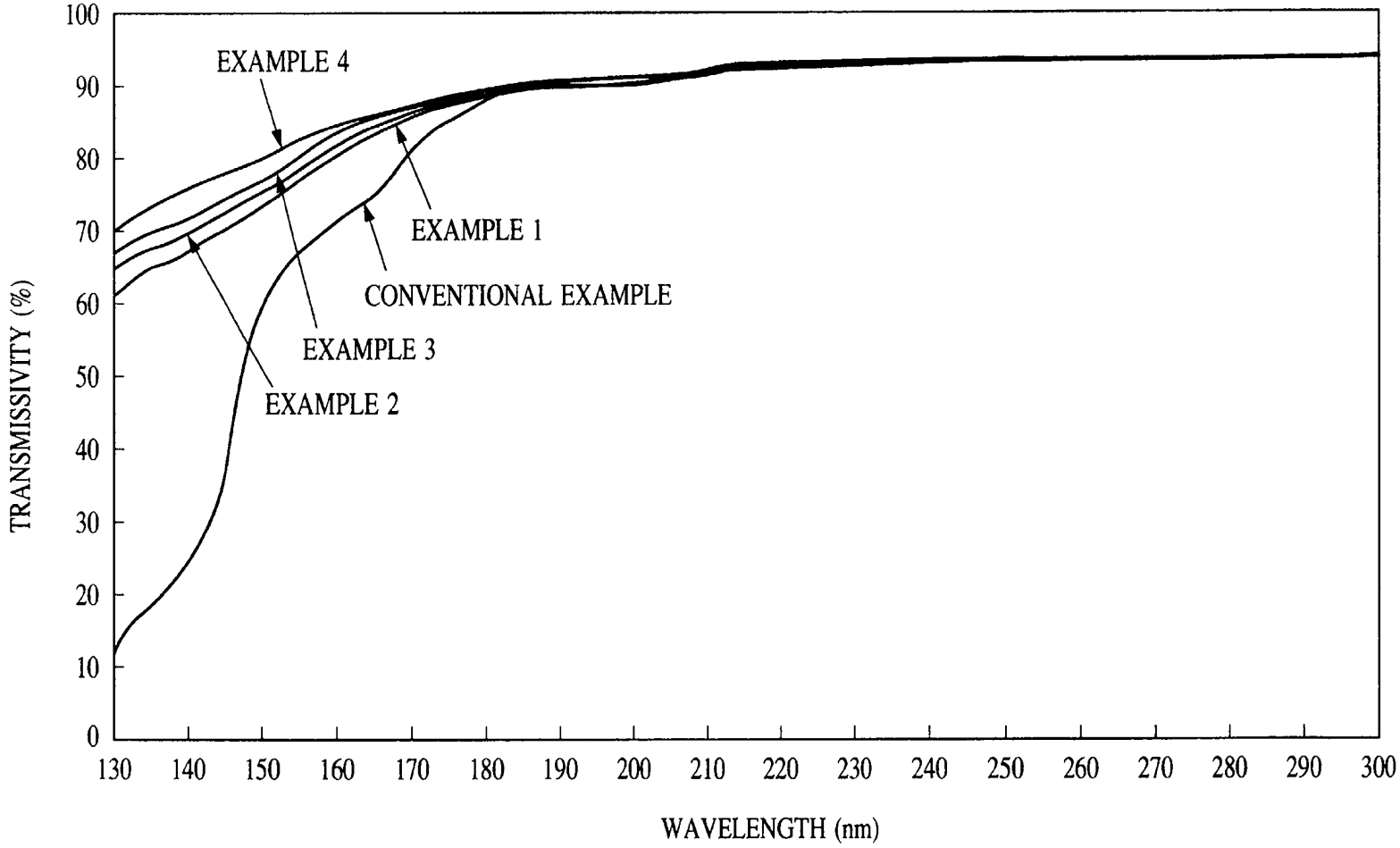
100
90
80
70
60
50
40
30
20
10
0
TRANSMISSIVITY (%)
EXAMPLE 4
EXAMPLE 1
CONVENTIONAL EXAMPLE
EXAMPLE 3
EXAMPLE 2
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
290
300
WAVELENGTH (nm)

FIG. 8

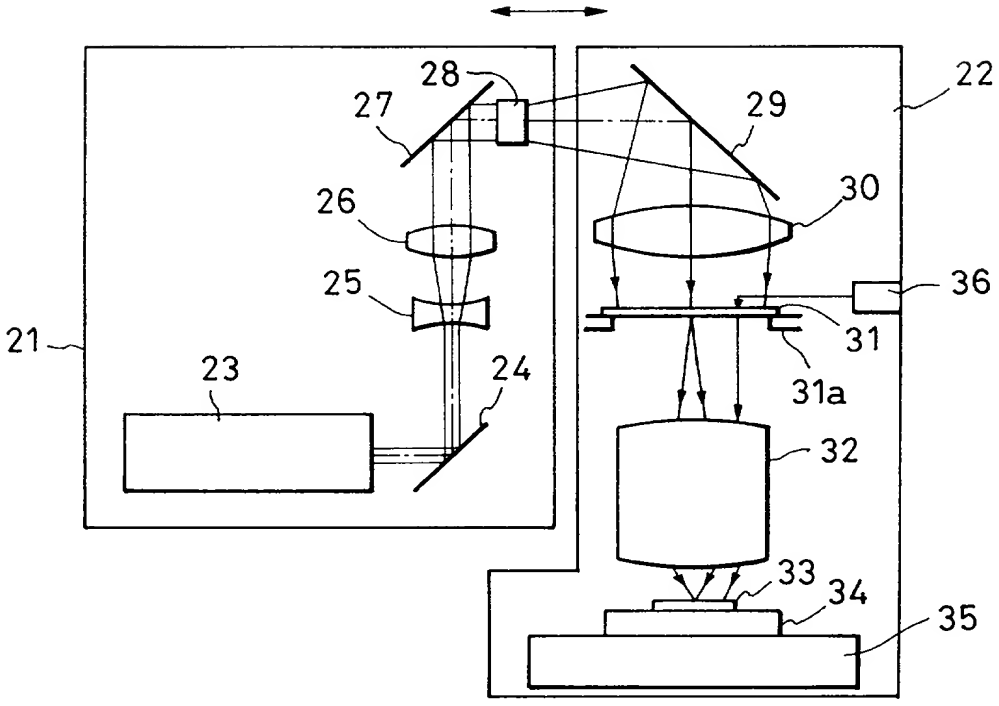

FIG. 9

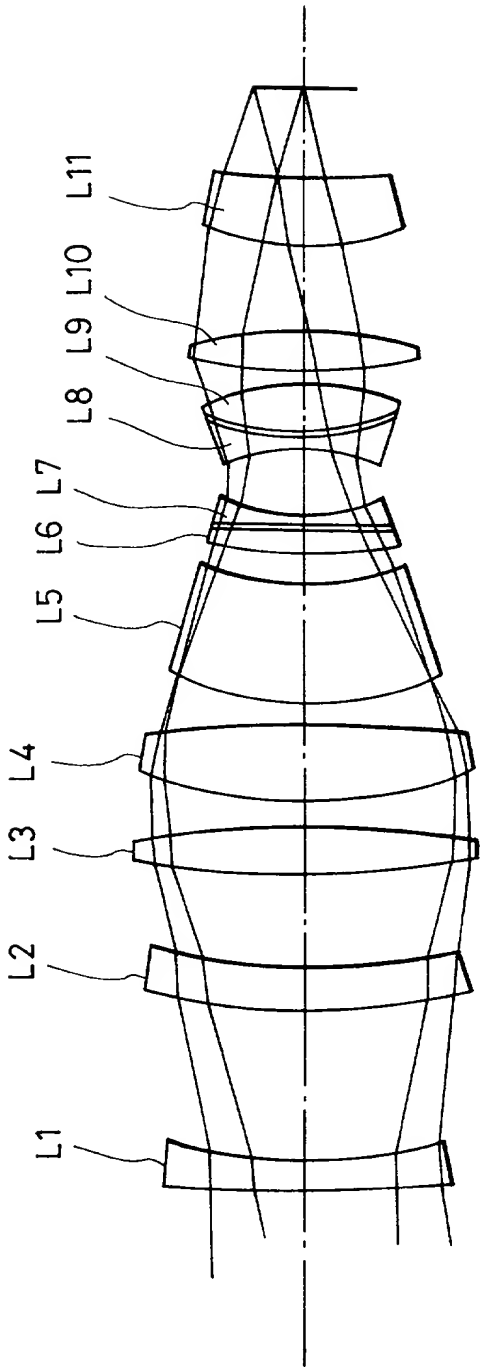

FIG. 10A

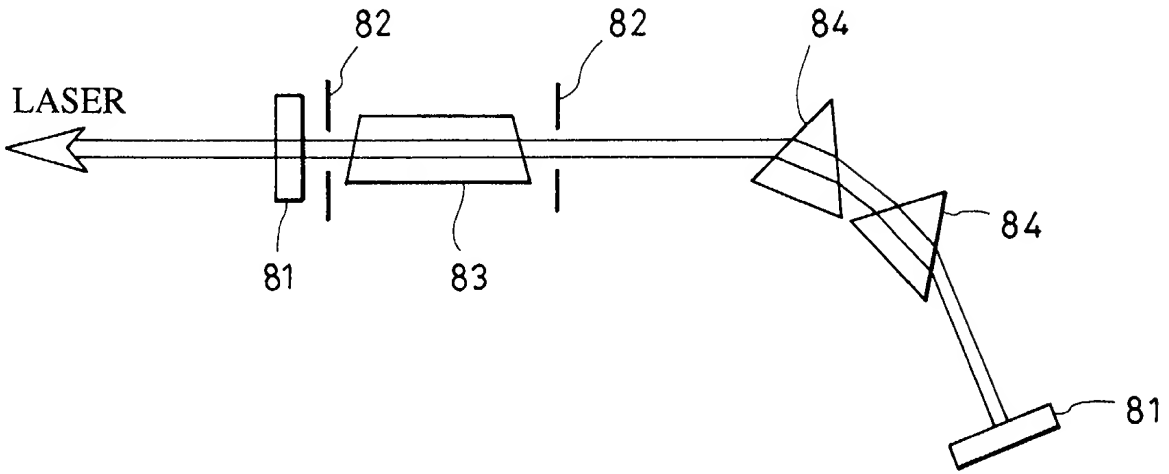

FIG. 10B

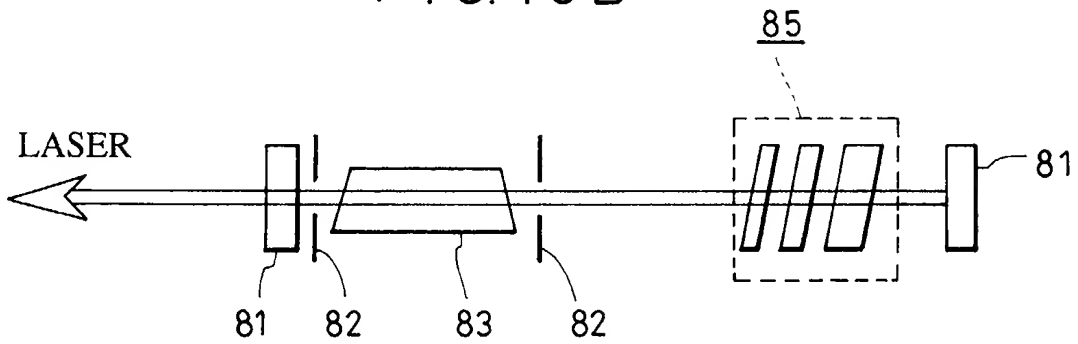

FIG. 11